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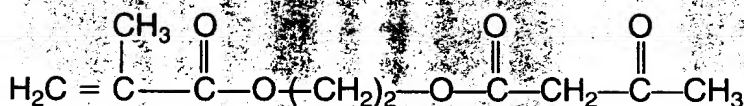
For the

MARKET



Acetoacetoxyethyl Methacrylate (AAEM)

Acetoacetyl Chemistry



The resins market has been characterized over the past few years by dramatic technical change. The combination of regulatory pressures and ever-changing performance requirements has led to many new chemistries and technologies. The use of the acetoacetyl group in resins offers a new approach to meeting some of today's regulatory and performance challenges.

The inclusion of acetoacetyl groups in a resin may be achieved by either polymerizing an acetoacetylated monomer, such as AAEM, into the polymer backbone, or acetoacetylating a hydroxyl-bearing polymer after synthesis. Acetoacetyl groups have been shown to reduce the solution viscosity and the glass transition temperature of resin systems, offering many benefits in polymer modification.

In addition to beneficial effects on resin properties, the acetoacetyl group also provides two reactive sites—an active methylene group and a ketone carbonyl group. These two sites make available many reactions that are useful for cross-linking or further modification of resins. The utility of acetoacetyl chemistry in resin modification and many of the reactions it makes possible are discussed in this publication.

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Acetoacetoxyethyl Methacrylate (AAEM)

CAS No. 21282-97-3

Typical Properties^a

Molecular Weight (C ₁₀ H ₁₄ O ₅)	214.22
Appearance	Clear, light yellow liquid
AAEM, %	97
2-Hydroxyethyl Methacrylate, %	2
Methacrylic Acid, %	0.3
Ethylene Glycol Dimethacrylate, %	0.4
Water, %	0.05
Inhibitor (BHT), ppm	1,000
Boiling Point	Polymerizes
Solubility	Miscible with most organic liquids

Q and e Values

Q	0.68
e	0.13

Reactivity Ratios

Monomer 1 (M ₁)	Monomer 2 (M ₂)	R ₁	R ₂
AAEM	Methyl Methacrylate	0.95	0.90
AAEM	Styrene	0.60	0.70

^aProperties reported here are typical of average lots. Eastman makes no representation that the material in any particular shipment will conform exactly to the values given.

Uses/Applications

The active methylene group and the ketone carbonyl in the acetoacetoxy portion of the molecule and the acrylic double bond provide three separate reactive sites for exploration in polymer development.

Samples

One-pint samples are available at no charge for planned technical evaluation.

Storage

Carbon steel 304SS and 316SS as well as aluminum are suitable materials for storage of AAEM. As with any reactive acrylate, store in a cool, dry area. Precautions such as tank cooling and insulation to protect vessels from local heating are suggested for bulk storage. Replenish headspace air every 6 months with inert gas containing between 4% and 9% O₂. Data from long-term storage stability tests are available on request.

Acrylic Resin Synthesis and Properties

Features

- Reduced Solution Viscosity
- Reduced Polymer T_g
- Good Acrylic Reactivity
- Cross-Linking Versatility Through Multiple Reaction Pathways
- Improved Adhesion Through Metal Chelation
- Reactive Pathways for Further Polymer Modification

AAEM is a higher-molecular-weight methacrylic monomer possessing a pendant acetoacetoxyethyl group. This long tail modifies the physical properties of acrylic polymers by decreasing solution viscosity and lowering the glass transition temperature. In addition, the acetoacetyl group contains an active methylene and a carbonyl group, which can be used to further modify or cross-link the polymer. AAEM is useful where increased nonvolatile content, cross-linking versatility, or reduced glass transition temperatures are required.

In considering the use of a methacrylic monomer, characteristics such as effect on solution viscosity, effect on glass transition temperature, and acrylic reactivity are important to the resin formulator. AAEM performs well in all of these areas.

Solution Viscosity

Lower solution viscosity is the key to obtaining higher-solids coatings. The inclusion of AAEM in acrylic polymers adds a long, bulky pendant group to the polymer chain, giving increased separation between chains. The added separation and the fact that AAEM contains no hydroxyl functionality¹ combine to minimize hydrogen bonding between polymer chains, leaving the polymer chains more mobile and decreasing solution viscosity.

To illustrate the effect of AAEM on solution viscosity, a series of acrylic resins were prepared based on methyl methacrylate (MMA) with increasing amounts of AAEM. The resin composition, physical properties, and synthesis procedure are given in the following tables.

¹While AAEM does not contain hydroxyl groups, it is still capable of reaction with conventional melamine and isocyanate cross-linkers. See Eastman Publication N-322 for details.

MMA/AAEM Resins and Properties

Resin Reference	A	B	C	D	E	F
Mole % AAEM	0	10	20	30	40	60
Wt % AAEM	0	19.2	34.9	47.8	58.8	76.2
M_n	9,585	8,818	6,967	7,650	8,930	9,396
M_w	50,215	15,697	13,750	22,027	21,437	18,768
$T_g, ^\circ\text{C}$	105	84	57	51	44	32
Determined % Solids ^a	59.0	58.8	57.7	58.0	56.4	56.4
Brookfield Viscosity, mPa·s (thousands)	471	282	42	24	16	6
Initiator: 1.5% Vazo 67 ^b						

^aIn Eastman EEP solvent (ethyl 3-ethoxypropionate)

^bDu Pont

Resin Synthesis

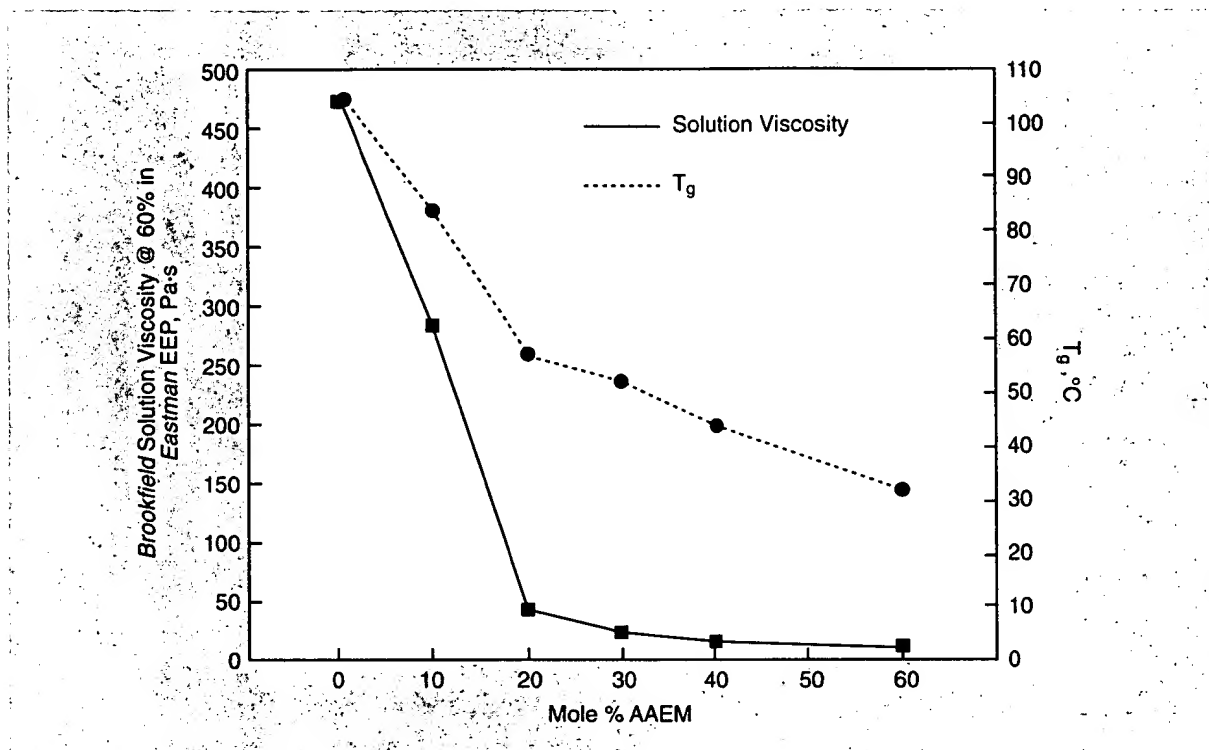
Reaction setup: Four-neck round-bottom flask equipped with (a) heating mantle, (b) air-driven stirrer, (c) nitrogen purge, (d) thermocouple and thermowatch electronic temperature control, (e) condenser, (f) addition funnel.

Synthesis Procedure

1. Place *Eastman* EEP solvent in flask and heat to 100°C.
2. Mix monomers and initiator to complete dissolution. Place mixture in addition funnel and add dropwise to heated solvent over a 4- to 4½-hour period.
3. After addition of monomer mix is completed, let reaction continue at 100°C for ½ hour.
4. Dropwise add an additional ½ mole % initiator as a 10% solution in the *Eastman* EEP solvent over a 10- to 15-minute period to terminate the reaction.
5. Turn heat off and transfer resin to storage container.

The viscosity data shown below illustrate the dramatic decrease in solution viscosity with increasing AAEM concentration. It should be noted that the major portion of the viscosity reduction occurs with the addition of the first 20-mole % of AAEM.

Effect of Acetoacetyl Groups on Resin Properties (Solution Viscosity and T_g)



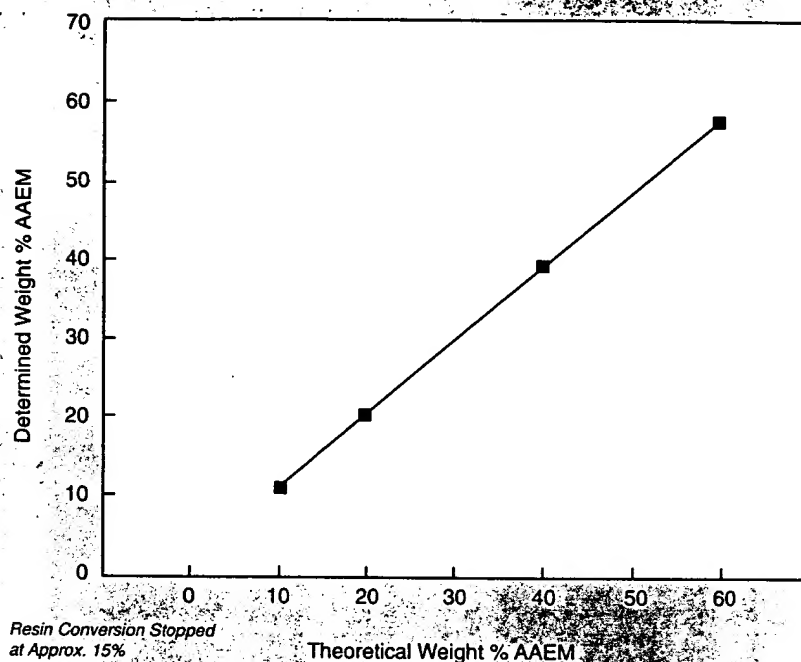
Glass Transition Temperature

The same increased chain separation and reduced hydrogen bonding characteristics of AAEM that give reduced solution viscosity also lead to lower glass transition temperature (T_g). The T_g was measured for the series of model resins described on page 5 using differential scanning calorimetry inflection point. The results, as seen in the previous graph, illustrate the reduction in T_g with even small amounts of AAEM. Lower T_g s are often equated to improved impact resistance in acrylic coatings resins.

Acrylic Reactivity

The reactivity of AAEM has been compared with an industry standard, methyl methacrylate (MMA), using a series of copolymers produced from monomer mixes prepared at 90/10, 80/20, 60/40, and 40/60 weight % ratios. Conversion was terminated at approximately 15%, and resin samples were analyzed for monomer content by nuclear magnetic resonance.

AAEM Reactivity



This figure shows a plot of theoretical versus determined weight % AAEM in the copolymers. An approximate 1:1 relationship exists between the theoretical and determined amounts of AAEM in the MMA copolymer, indicating that AAEM and MMA have similar degrees of reactivity in acrylic synthesis reactions.

Innovative Cross-Linking Pathways and Reactions of Acetoacetylated Polymers

Acetoacetyl groups that are attached to a polymer can be used to modify or cross-link that polymer. This technology is receiving considerable attention from the plastics, coatings, and specialty polymers industries. A brief overview of the chemistry of the acetoacetyl group is presented here with special emphasis on those reactions that can be used to modify acetoacetylated polymers.

Acetoacetylated polymers can be prepared by polymerizing an acetoacetylated monomer such as AAEM into the polymer chain or by acetoacetylating a polymer after synthesis. Polymers such as hydroxylated polyesters can be acetoacetylated with diketene, the diketene-acetone adduct (TKD), methyl acetoacetate or ethyl acetoacetate.

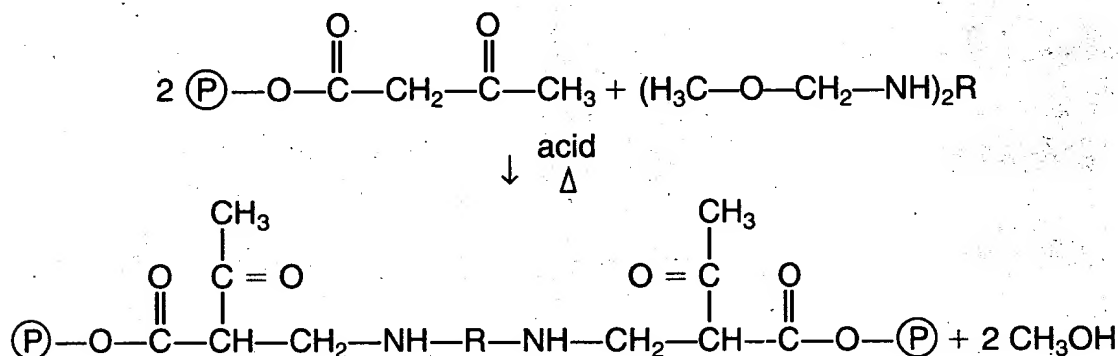
There are two reactive sites on a polymer-anchored acetoacetyl group that can be used to form derivatives of the polymer: the active methylene group (CH_2) and the ketone carbonyl group ($\text{C}=\text{O}$).

Melamines

The active methylene group will react with melamines under conditions similar to those required for the reaction of hydroxyls with melamines. The temperature required for reaction will depend on the choice of melamine. A fully methylated melamine requires a temperature of 150°C (300°F) plus an acid catalyst.

Reaction With Melamine at the Active Methylene Group

Ⓟ = polymer backbone

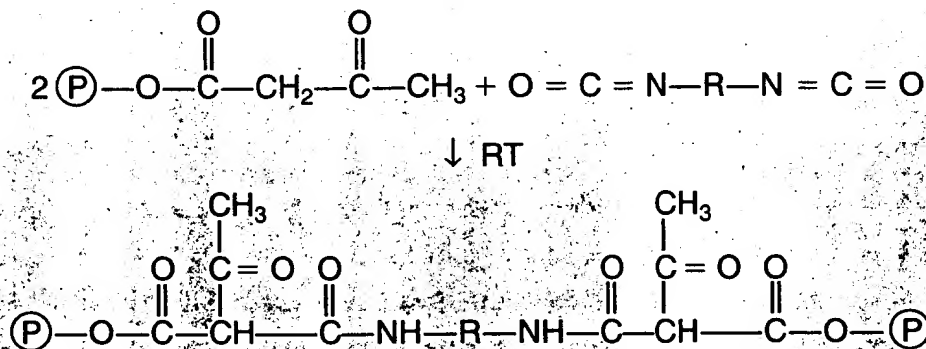


It should be noted that, unlike the reaction of hydroxyl-functional resins with melamines, which forms an ether linkage, the reaction of the methylene group with melamines forms a carbon-carbon bond.

Isocyanates

The active methylene group will react with free isocyanates at ambient temperature and with blocked isocyanates at elevated temperature in a manner similar to the reaction of isocyanates with hydroxyls. This reaction proceeds as seen below.

Reaction With Isocyanate at the Active Methylene Group

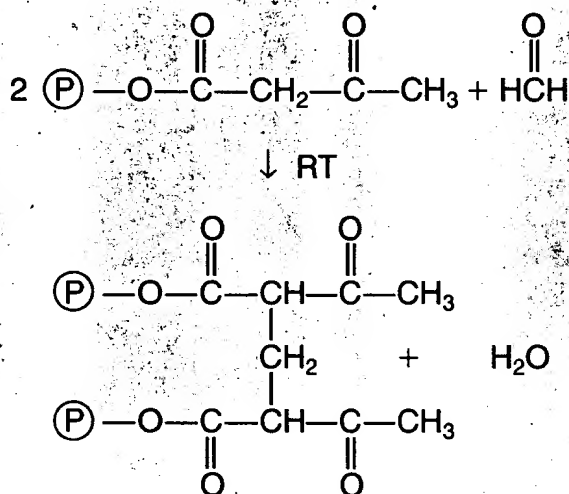


This reaction forms a nitrogen-carbon-carbon linkage as opposed to the typical nitrogen-carbon-oxygen urethane linkage.

Aldehydes

Aldehydes, especially formaldehyde, rapidly condense with the active methylene group of acetoacetylated polymers. This reaction can also be used to form bridges between proximate methylene groups and can, therefore, be used to cross-link linear polymers into thermoset materials as illustrated by the next figure.

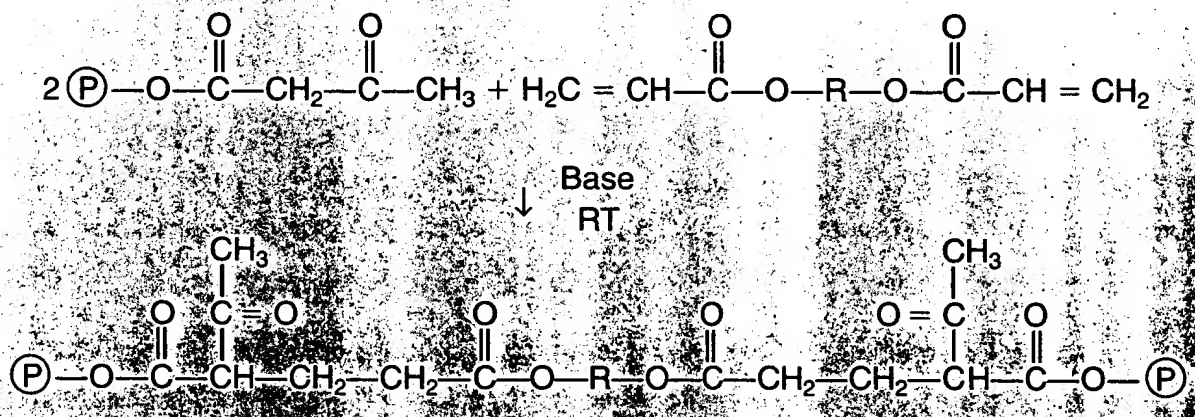
Reaction With Aldehyde at the Active Methylene Group



Michael Reaction

The Michael reaction can also be used to functionalize or cross-link acetoacetylated polymers. In this reaction, the methylene group is deprotonated with a strong base and then reacted with an electron-deficient olefin. Similarly, the methylene group can be alkylated with an alkyl halide in the presence of a strong base.¹ The use of polyfunctional alkylating reagents would provide cross-linked polymers.

The Michael Reaction at the Active Methylene Group

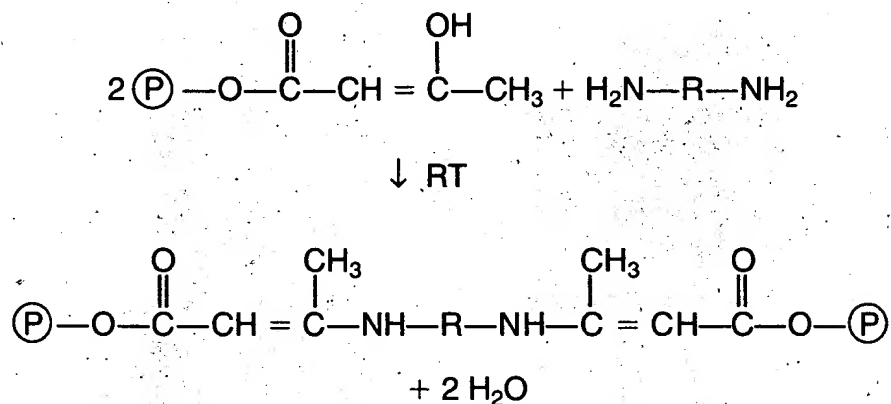


¹See Eastman Publication N-324 for a comparison of catalysts for cross-linking acetoacetylated resins via the Michael reaction.

Enamine Formation

Enamines can be prepared by the reaction of amines with carbonyl groups. Diamines can be used in this reaction to cross-link acetoacetylated polymers.

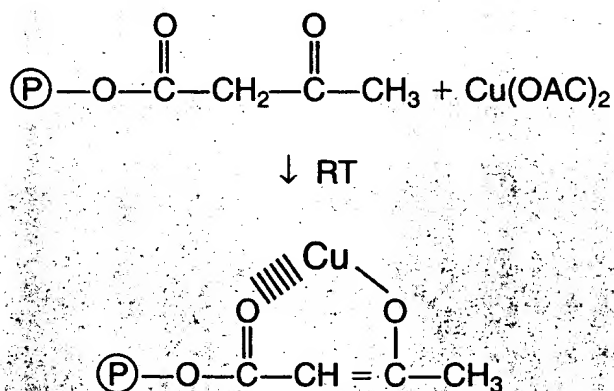
Enamine Formation at the Carbonyl Group



Chelation

The carbonyl group of acetoacetylated polymers is in equilibrium between its keto and enol forms. This enolization enables acetoacetylated polymers to chelate with metals such as zinc, tin, lead, aluminum, copper, and zirconium. Polyvalent cations can be used for cross-linking purposes.

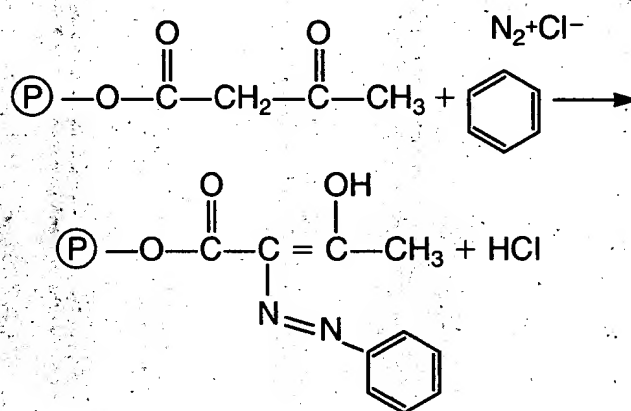
Chelation Reaction at the Carbonyl Group



Diazonium Salts

One common application of acetoacetylated polymers is the preparation of colorfast fibers via the reaction of diazonium salts with the active methylene group on the polymer. The azo-dye that results from this coupling reaction is directly attached to the polymer, as illustrated here.

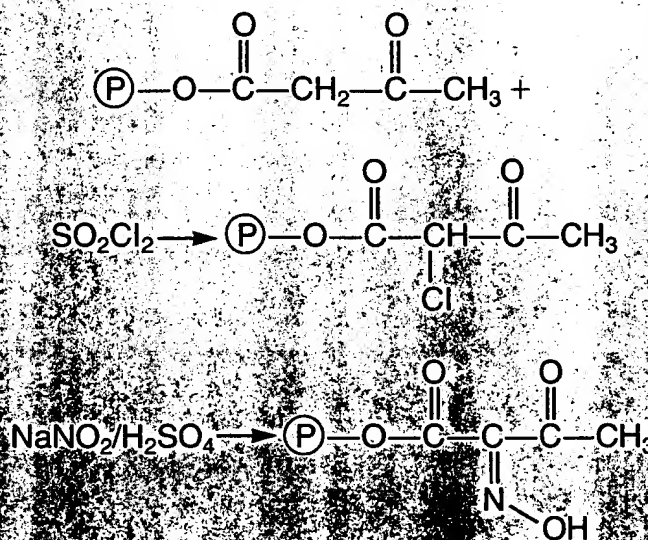
Reaction With Diazonium Salts at the Active Methylene Group



Derivatives

There are other ways to form derivatives with the active methylene group of acetoacetylated polymers. For example, the methylene group can be halogenated with sulfonyl chloride or nitrosated with nitrous acid. The resulting materials could be modified further, thus making a wide array of polymers available from a common starting material.

Derivation of Acetoacetates at the Active Methylene Group



Summary

AAEM is a methacrylic monomer that incorporates desirable polymer properties into acrylic resins. The bulky acetoacetoxyethyl pendant group increases chain separation and minimizes hydrogen bonding, which results in acrylic resins with lower solution viscosities and reduced T_g . The versatility of the acetoacetyl group makes possible many reactions for cross-linking or modification of polymer systems. In addition, metal chelation offers opportunities for improved adhesion and corrosion resistance for metal coatings. With all these advantages, AAEM has much to offer in both solution- and emulsion-produced acrylic resins.

Eastman Publication N-322 contains more information on the use of some of the cross-linking reactions for coatings resins. In general, this area of polymer chemistry is underdeveloped, but it promises considerable rewards in the form of new performance polymers for the future.

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